



Studies on the faradaic efficiency for electrochemical reduction of carbon dioxide to formate on tin electrode



Weixin Lv, Rui Zhang, Pengran Gao, Lixu Lei*

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China

HIGHLIGHTS

- pH value in CO₂-saturated KHCO₃ solution has an effect on CO₂ reduction.
- Oxidation of formate is main reason for efficiency decreasing with time lasted.
- Formate oxidization accelerates as formate concentration in electrolyte increases.
- Faradaic efficiency is >91% when formate concentration is <0.01 mol L⁻¹.

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ABSTRACT

The electrochemical reduction of carbon dioxide (CO₂) on Sn electrode has been investigated in aqueous KHCO₃ solution by cyclic voltammetry and controlled potential electrolysis. The results show that the faradaic efficiency for producing formate is affected by the electrolysis potential, the concentration and pH value of KHCO₃ solution; the reason for the decrease of faradaic efficiency as the electrolysis time lasts is the oxidation of formate on the Pt anode. When the concentration of the formate in the electrolyte is less than 0.01 mol L⁻¹, the faradaic efficiency can reach above 91%.

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1. Introduction

The transformation of CO₂ into value-added chemicals and fuels has attracted much attention in recent years. Up to now, many chemical, photochemical, electrochemical and photoelectrochemical methods have been investigated for the purpose [1–5]. Among these routes, electrochemical reduction of CO₂ is a promising process because the product can be selectively controlled by changing the electrolysis condition, such as electrode [6–10] and electrolyte [11,12]. To date, formic acid [13], carbon monoxide [14], methanol [15], and oxalic acid [16] have been prepared by this way. Electrochemical reduction of CO₂ also supplies a route that makes full use of the renewable photovoltaic, wind and marine energies that depend seriously on weather [17,18].

The electrode materials include various pure metals, coordination compounds or alloys, which play very important roles in

determination of the products [19–26]. For example, Sn, Pb, Hg and In electrodes tend to produce formate in aqueous solution with high faradaic efficiency [27,28]. It is very interesting that faradaic efficiency for formic acid production in electrochemical reduction of CO₂ in aqueous KHCO₃ solution in a fixed-bed reactor was 90% at 30 min, but it decreased to 30% after 2 h. The reason for this decrease was suggested to be the oxidation of formic acid [29]. However, another report revealed that the decrease should be resulted from the deposition of Zn on the surface of Sn electrode during electrolysis [30]. These two reports have provided different explanations for the decrease of faradaic efficiency.

Agarwal et al. discussed the engineering and economic feasibility of large-scale electrochemical reduction of CO₂ to formate, and suggested that this process can be operationally profitable [31]. Therefore, it is important to find out what exactly determines the faradaic efficiency of the electrochemical reduction of CO₂.

In this paper, Sn was chosen from the metals with high faradaic efficiency for producing formate because of its low cost and relatively low toxicity. The influences of key variables like the electrolysis

* Corresponding author. Tel.: +86 25 5209 0620x6421; fax: +86 25 52090618.
E-mail address: lixu.lei@seu.edu.cn (L. Lei).

potential, the concentration and pH value of the KHCO_3 solution on the faradaic efficiency for producing formate were studied to obtain the optimal electrolysis condition. The most importantly, it is to find out the reason why the faradaic efficiency decreases.

2. Experimental

All the materials were purchased ($\geq 99.5\%$) from commercial companies, and used without further treatments.

Scanning electron microscope (SEM) images were taken with a Hitachi S-4800 microscope at an acceleration voltage of 15 kV. The pH values of all the electrolytes were determined by a pen-like pH meter (CT-6022, Shanghai Rentong Meter Co., Ltd., China).

The products in the electrolyte were directly analyzed by ion chromatography (ICS-900 Dionex). The column was an IonPac AS11-HC anionic column using 0.02 mol L^{-1} KOH as the mobile phase at the rate of 1 mL min^{-1} . $10 \mu\text{L}$ of the electrolyte were used for each time. The amount of formate in the electrolyte was also determined by titration (see Supporting information for details).

The cell used here is an airtight and undivided glass cell equipped with a gas inlet and outlet which is able to pass the either N_2 (99.99%) or CO_2 (99.99%) through the solution. A conventional three-electrode system was used during the measurements. The working electrode was always a Sn plate with a geometric surface area of 1 cm^2 . To obtain repeatable results, each Sn plate electrode is used only once. A Pt plate ($1 \times 1 \text{ cm}^2$) and an Ag/AgCl electrode (sat. KCl) were used as counter and reference electrodes, respectively. The electrolyte used was 40 mL of KHCO_3 aqueous solution. All experiments were performed under room temperature and ambient pressure.

Cyclic voltammetry (CV) experiments were carried out using a CS350 electrochemical workstation (Wuhan CorrTest Instrument Co., Ltd., China) after purging the solution with either N_2 or CO_2 for 30 min for the actual determinations. The current density (j) is determined on the geometrical area of the electrode.

Controlled potential electrolysis was carried out using a LAND CT2001C cell performance-testing instrument (Wuhan Electronics Co., Ltd., China) in the same three-electrode electrochemical cell. The electrolyte was saturated with CO_2 before each electrolysis process, and CO_2 gas was continuously aerated at a flow rate of 10 mL min^{-1} during the electrolysis process. The electrolysis experiments were terminated when the total charge passed reached a certain value. The average current density (j_a) is expressed as the total current divided by the geometric surface area of the Sn electrode (1 cm^2) for all cells.

The faradaic efficiency for the formation of formate (f) is determined by Equation (1):

$$f = n_{\text{formate}} nF/Q \quad (1)$$

where n_{formate} is the moles of the formate produced; n represents the number of electrons required for the formation of one molecule of formate from CO_2 ($n = 2$ here); F is Faraday's constant (96485 C mol^{-1} of electrons); and Q is the total charge in Coulomb passed across the electrode during the electrolysis.

3. Results and discussion

3.1. CV measurements

Fig. 1 depicts the voltammograms of the Sn electrode in 0.1 mol L^{-1} KHCO_3 solution after being bubbled with N_2 or CO_2 for 30 min. The anodic peaks between -0.3 and -0.6 V and the cathodic peak between -0.8 and -1.1 V in CV curves can be attributed to the formation and the reduction of tin oxides in basic

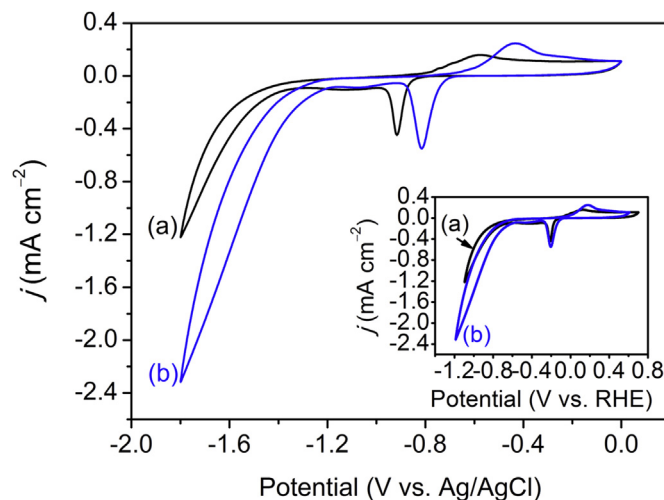


Fig. 1. Cyclic voltammograms on the Sn electrode in 0.1 mol L^{-1} KHCO_3 solution after being bubbled with N_2 (a) and CO_2 (b) for 30 min. The inset is the same cyclic voltammograms based on the RHE reference scale. The scan rate was 0.05 V s^{-1} .

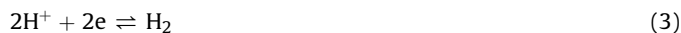
media respectively [32]. On the cathodic end of the voltammograms, sharp increases of the current densities can be observed under both N_2 and CO_2 (curves a and b in Fig. 1), which should be most probably caused by the reduction of water (under N_2) and CO_2 (under CO_2).

Theoretically, it can be predicted that the pH value of the KHCO_3 solution will be lowered if the solution is saturated with CO_2 because of the reaction (2):



Experiments did show that the pH value of the KHCO_3 solution increases continuously if it is bubbled with N_2 because of the dissipation of CO_2 , but it decreases if it is saturated with CO_2 (see Tables S1 and S2 in Supporting information for details). If the KHCO_3 solution has been bubbled with N_2 and CO_2 for 30 min, the pH values are 8.69 and 6.98 respectively.

As the pH value seriously affects the electrode potentials for the reduction of H_2O and CO_2 :



the CV curves should be adjusted to exclude the effect of pH. By converting the reference scale from Ag/AgCl to RHE using $E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + 0.1988 \text{ V} + 0.0591 \text{ V} \times \text{pH}$, the cyclic voltammograms is re-plotted in the inset of Fig. 1. It can be seen that peaks related to the formation and the reduction of tin oxides almost overlapped [32]; and in the left end, the potential at the same current under CO_2 is 0.1 V higher than that under N_2 , and the current density at the same potential for the latter is about twice of that for the former. The increase of cathodic current can only be caused by the reduction of water under N_2 , but the enhanced current can be caused by both the reduction of CO_2 and H_2O under CO_2 . We tried to find out if there is any substance that can reduce KMnO_4 in strong alkaline solution, and found that the solution after 5 circles of the CV scan under CO_2 contained the substance that made the color change from purple, characteristic of KMnO_4 , to the green color of K_2MnO_4 in a few minutes; however, that under N_2 did not. Therefore, a small amount of formate formed.

3.2. Faradaic efficiency for electrochemical reduction of CO₂ to formate

According to the results shown in Fig. 1, electrolysis experiments were performed in CO₂-saturated 0.1 mol L⁻¹ KHCO₃ solution applying a constant potential in the range from -1.4 to -2.2 V (vs. Ag/AgCl) at 0.2 V intervals, during which CO₂ was continuously bubbled into the electrolyte solution, and the results are shown in Fig. 2. It can be seen that the average current density increases as the cathode potential decreases from -1.4 to -2.2 V, however, the faradaic efficiency for producing formate increases at first until -1.8 V, where it reaches the maximum. As the potential decreases further, the faradaic efficiency begins to decrease. We can see during the experiments that bubbles form and increase fast on the surface of Sn cathode, which can be certainly attributed to the enhancement of H₂ evolution at more negative potentials. This is consistent with the literature [27,29,33].

It is known from Fig. 2 that the appropriate electrolysis potential for efficient production of formate should be around -1.8 V vs. Ag/AgCl. In order to determine the optimal electrolyte concentration, a series of electrolysis experiments at -1.8 V vs. Ag/AgCl were carried out in CO₂-saturated KHCO₃ solutions with different concentrations, during which CO₂ was bubbled into the electrolyte continuously. It can be seen from Fig. 3a, with the increasing concentration of the electrolyte, although the average current density increases, the faradaic efficiency for producing formate decreases. The faradaic efficiency produced in 0.1 mol L⁻¹ KHCO₃ solution is the highest. This is also consistent with the literature [30].

Fig. 3b shows pH values of the electrolyte solutions before and after saturating with CO₂. After CO₂ saturation, the pH value of each KHCO₃ solution decreases because of the reaction (2), and it also decreases as the concentration of the KHCO₃ solution decreases. The faradaic efficiency for producing formate decreases as the pH value of KHCO₃ solution increases (see Fig. S2). CO₂-saturated solution containing less concentration of KHCO₃ possesses higher concentration of H⁺. Wu et al. considered the effect of concentration of H⁺ at the electrode surface, [H⁺]_{surface}, on the production of formate, and pointed out that the faradaic efficiency for producing formate is promoted by the existence of H⁺, because it is a necessary reactant for producing formate [30]. [H⁺]_{surface} is a function of the potential of the outer Helmholtz Plane, *E*, and can be given as

$$[H^+]_{\text{surface}} = [H^+]_{\text{bulk}} e^{-\frac{FE}{RT}} \quad (5)$$

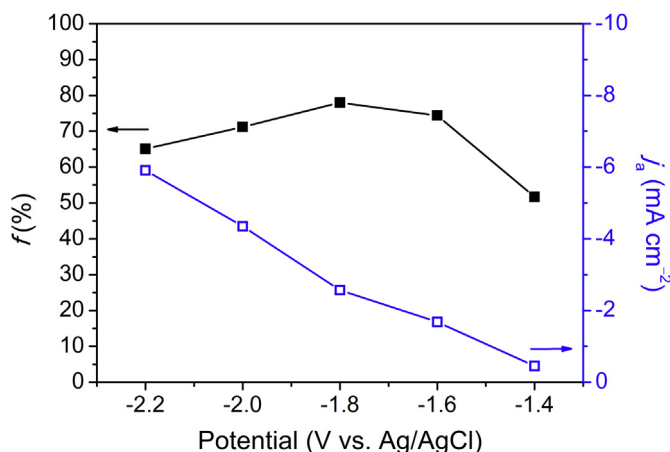


Fig. 2. Variations in the faradaic efficiency (■) and the average current density (□) for producing formate with electrolysis potential. The total charge passed was 100 C.

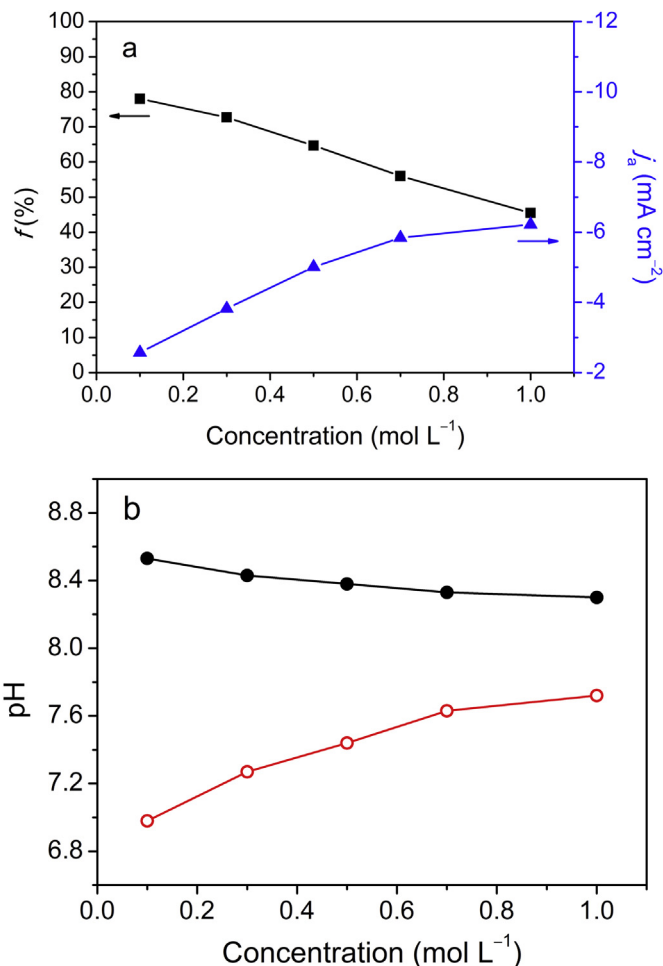


Fig. 3. (a) Variations in the faradaic efficiency (■) and the average current density (□) for producing formate with the concentration of KHCO₃, the cathode potential was maintained at -1.8 V vs. Ag/AgCl, and the total charge passed was 100 C. (b) Plots of the pH value against the concentration of KHCO₃ in electrolyte before (●) and after (○) saturating with CO₂.

where *E* is defined with respect to the potential in the bulk solution [30]. When the electrochemical reduction of CO₂ proceeds under a constant potential, the [H⁺]_{surface} increases with the [H⁺]_{bulk}. This explains why KHCO₃ solution of lower concentration results in higher faradaic efficiency. We have also measured the pH value after the electrolysis, and the value is approximately equal to the initial pH value (saturated with CO₂). This means that CO₂ is consumed, but HCO₃⁻ remains there, consequently, the [H⁺]_{bulk} does not change. This is in consistency with the total reaction (6), in which CO₂ reacts with H₂O to produce HCOOH on the cathode and O₂ on the anode:



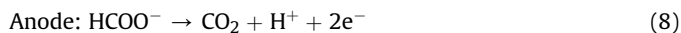
3.3. Relationship between the faradaic efficiency and the electrolysis time

It has been reported that the faradaic efficiency for producing formate changes with the electrolysis time, which has been explained based on the oxidation of formate on anode or the contamination of Sn cathode by impurity [29,30,34]. To verify those observations, we have taken SEM images of the cathode before and after the electrolysis, and studied the time-dependent faradaic efficiencies. Fig. 4 shows the SEM images and the EDS spectra of the

Sn electrode before and after the cathodic reduction of CO₂ for 40 h. It can be seen that the electrode becomes much coarser after electrolysis, but there is no difference on the EDS spectra. Consequently, we were not bothered by impurities. In fact, those possible impurities that may interfere the electrolysis can be removed by pre-electrolysis, therefore, they should not be a problem [34,35].

As we had known that we were not bothered by impurities, we were more interested to find out how the oxidation of formate on anode affects the efficiency by time-dependent research. Fig. 5 shows the variations of the faradaic efficiency and the current density with electrolysis time during the electrochemical reduction of CO₂ at −1.8 V vs. Ag/AgCl for 40 h. As it was observed before [29,30], high faradaic efficiency is observed during the initial 6 h of electrolysis, but the efficiency decreases significantly after then. When the time lasts for 40 h, the faradaic efficiency is only 41.7%. In spite of that, the current density remains almost unchanged, which may means that the nature of the cathodic reaction is not changed.

To find out why the faradaic efficiency lowers as time prolongs, we carried out the electrolysis in 0.1 mol L^{−1} KHCO₃ solution with pre-added sodium formate under static air or CO₂. As before, the electrolysis tests were performed at −1.8 V vs. Ag/AgCl, and the anode is a Pt plate. Fig. 6a is the measured concentration of formate without electrolysis; Fig. 6b and c shows the measured concentration of formate after electrolysis of 200 C under static air and CO₂, respectively. It can be seen that consumption of formate occurs if the electrolysis is carried out under static air, but more formate produces if the electrolysis is carried out under CO₂ when the pre-added formate is in lower concentration. If the electrode reactions are solely as follows:



200 C of charge may cause 1.04 mmol of formate to be formed on the cathode or destroyed on the anode, which means an increase or

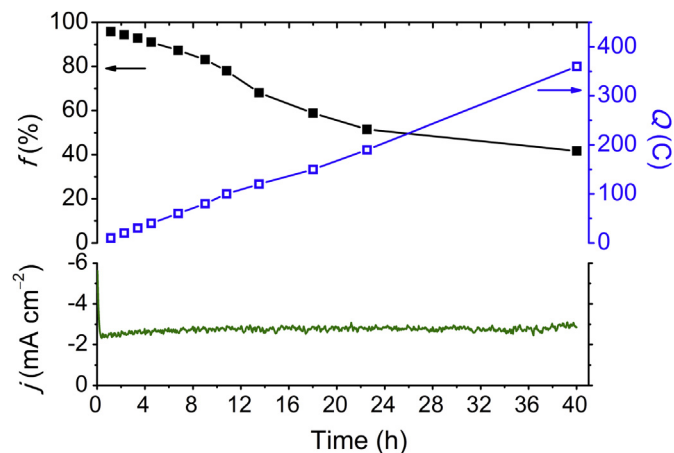


Fig. 5. Variations of the faradaic efficiency for producing formate (■), the charge passed (□) and the current density with electrolysis time during the electrochemical reduction of CO₂ in 0.1 mol L^{−1} KHCO₃ solution at −1.8 V vs. Ag/AgCl for 40 h.

decrease of 0.026 mol L^{−1} in the concentration of formate. Obviously, there is no such a big change; therefore, there must be some other processes occurred. For the electrolysis under static air, the most probable process is the electrolysis of water, which produces H₂ on the cathode and O₂ on the anode, but they have no effects on the concentration of formate besides consuming electricity. O₂ may be weakly reduced on the cathode, but it cannot change the concentration of formate. Consequently, we can conclude that the cathode reaction is reduction of water, but the anode reactions are oxidations of both water and formate. On the other hand, for the electrolysis under CO₂, although more formate is formed on the cathode, but even more formate is oxidized on the anode. This is in accordance with Fig. 5, which shows that the faradaic efficiency is lower than 50% when the total charge reaches 200 C. Here, the faradaic efficiency is further lowered because there are great amounts of formate before electrolysis.

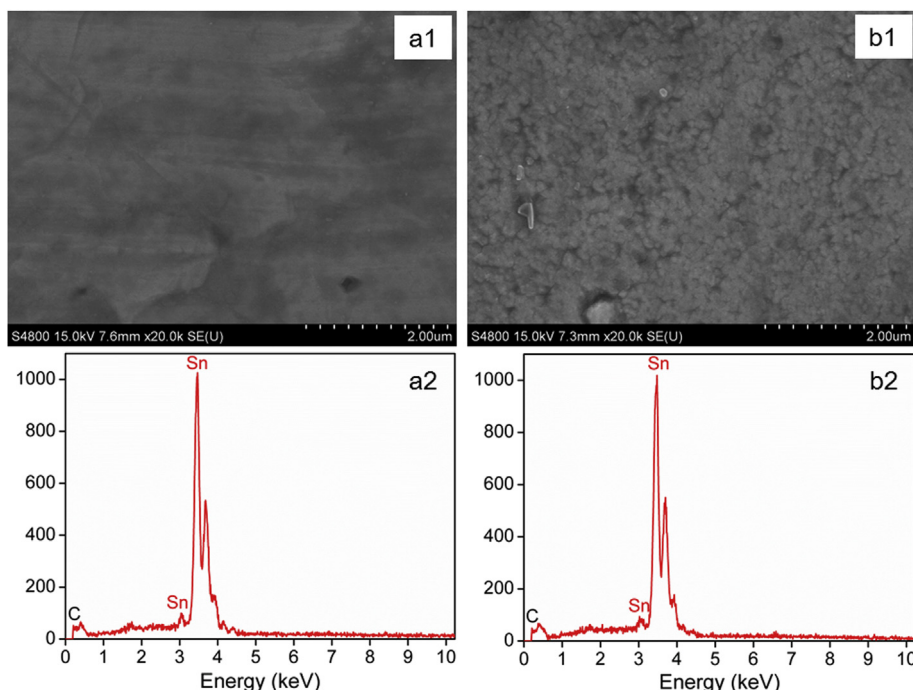


Fig. 4. SEM images and EDS spectra of the Sn electrode before (a1, a2) and after (b1, b2) the electrochemical reduction of CO₂ in 0.1 mol L^{−1} KHCO₃ solution for 40 h.

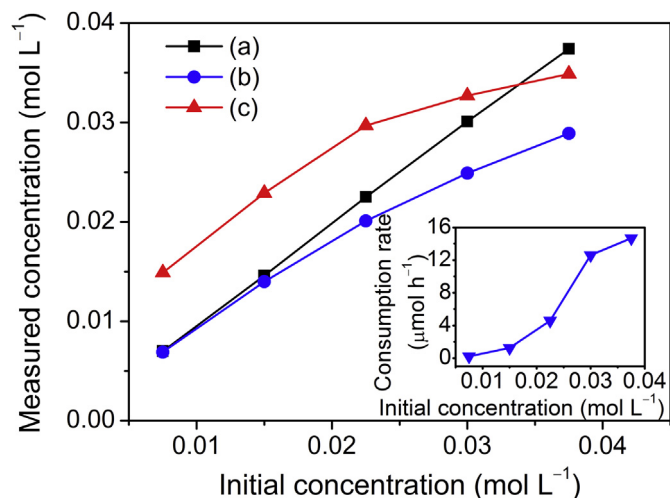


Fig. 6. Measured concentration of formate in the 0.1 mol L⁻¹ KHCO₃ solution containing different amount of formate before electrolysis (a) and after electrolysis of 200 C at -1.8 V vs. Ag/AgCl under static air (b) and CO₂ (c). The inset is the curve of formate consumption rate versus initial concentration.

The inset of Fig. 6 shows the relationship between the average consumption rate and the initial concentration of formate during the electrolysis. Obviously, oxidation of formate is much slow when its concentration is less than 0.015 mol L⁻¹, but it accelerates thereafter and again slows down after the initial concentration is higher than 0.03 mol L⁻¹. This means that the capacity of oxidation on the Pt anode is limited. Whatsoever, we do not like the formate produced on cathode being oxidized on anode, it is important to keep the concentration of formate as low as possible to realize the high efficiency.

Another experiment was carried out to confirm the above deduction, in which 100 mL of 0.1 mol L⁻¹ KHCO₃ solution was used instead of 40 mL of KHCO₃ solution. As shown in Fig. 7, the faradaic efficiency for the electrochemical reduction of CO₂ to formate maintains at 91% when the total charge reaches 200 C (equivalent to 0.01 mol L⁻¹ formate if the efficiency is 100%).

To keep the concentration of formate at a low level, measures have to be taken. Some researchers used H-type cell divided by a nafion membrane for electrochemical reduction of CO₂ to formic acid [6,36–38]. In this way, the problem of formic acid re-oxidization can be retarded but not solved, because nafion membrane cannot stop the diffusion of formic acid through it completely. For example, Narayanan et al. used In and Pb powders as the catalysts for electrochemical reduction of CO₂ to formate in a H-type cell. They found that the faradaic efficiency for producing formate in 1 mol L⁻¹ NaHCO₃ solution was as high as 80% after 300 s; however, the faradaic efficiency began to decline over a period of 1 h. They thought that the decrease of the faradaic efficiency during continuous operation was a result of the buildup of diffusion barriers resulting in the reduced availability of bicarbonate and CO₂ for reduction at the surface of the electrode [39].

We believe that could be worse if the faradaic efficiency is lowered by reduction of water, because it produces OH⁻ that converts CO₂ into HCO₃⁻, and HCO₃⁻ into CO₃²⁻. It is known that both HCO₃⁻ and CO₃²⁻ are anions which are difficult to reduce, and the dissolution of CO₂ could not be fast enough to compensate the loss of CO₂; therefore, reduction of water could make the reduction of CO₂ more difficult. Consequently, we have to study carefully all the factors that affect the reaction, and find out the best parameters for the operation.

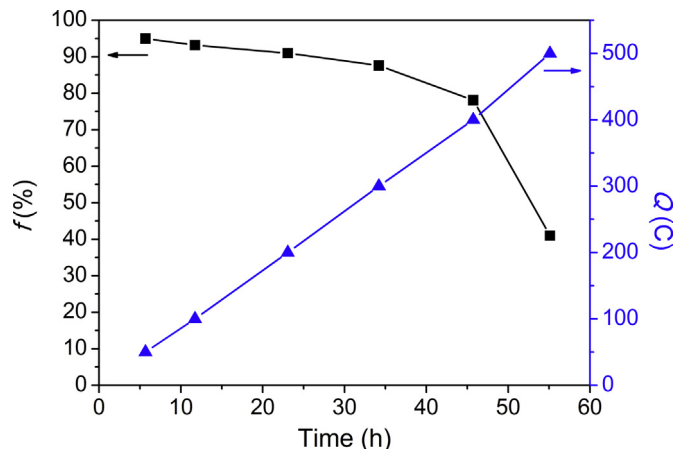


Fig. 7. Variations in faradaic efficiency for producing formate (■) and the charge passed (□) with the electrolysis time, when the electrochemical reduction of CO₂ was carried out in 100 mL of 0.1 mol L⁻¹ KHCO₃ solution at -1.8 V vs. Ag/AgCl.

4. Conclusions

In aqueous solution, electrochemical reduction of CO₂ often accompanies evolution of H₂; however, the reduction of CO₂ is easier than the evolution of H₂ on Sn electrode at the cathode potential in the range between -1.4 and -1.8 V vs. Ag/AgCl.

Faradaic efficiency for electrochemical reduction of CO₂ to formate is influenced by the cathode potential and the concentration and pH of the electrolyte. The cathode potential determines the current density on the electrode, and controls the H₂ evolution; the pH value of the electrolyte, controlled by the concentration of KHCO₃, also controls the faradaic efficiency for producing formate efficiently. It is found that the concentration of KHCO₃ as low as 0.1 mol L⁻¹ is good for the reduction of CO₂, which produces a slightly acidic environment (pH = 6.98). Even lower concentration of KHCO₃ is not suggested, as the current density is also lowered, which is not good for time efficiency.

The faradaic efficiency for producing formate is also deteriorated by high concentration of formate in electrolyte. This is because formate is oxidized on the anode especially when its concentration is too high (e.g. >0.034 mol L⁻¹). When the accumulated concentration is less than 0.01 mol L⁻¹, the efficiency could be higher than 91%.

Although it was found that impurity in electrolyte solution may affect the electrocatalytic activity of the electrode, we found it is not the case in our experiments. SEM images show that the surface of the Sn electrode become very coarse after electrolysis, but no impurity was found in EDS spectra. We believe that impurity should not be a problem, as we can remove them by pre-electrolysis or chemical treatments.

If reduction of water takes place, the pH of the electrolyte solution nearby the cathode will be higher which makes HCO₃⁻ and CO₂ less at the surface of cathode. Therefore, work on deterioration of H₂ evolution should be in need; using semipermeable film for conduction of proton or hydroxide ions may not help too much.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2013.12.063>.

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